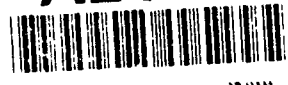


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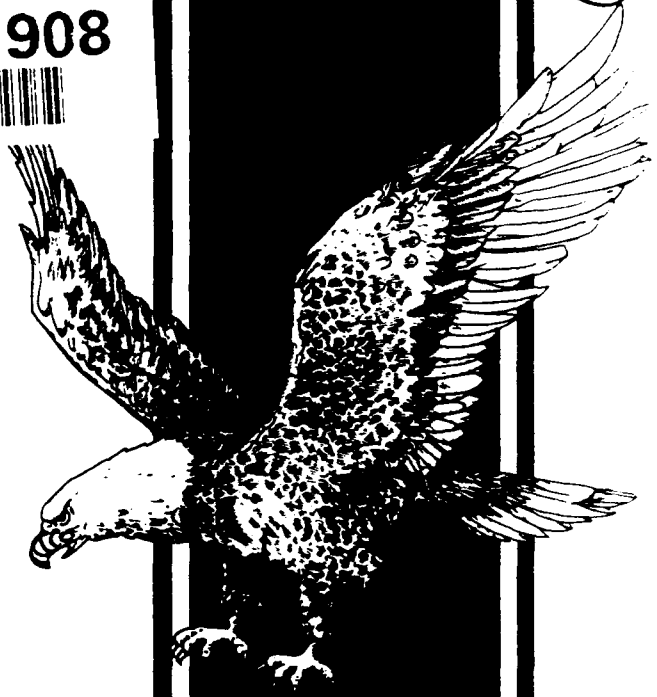
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# USATHAMA

U.S. Army Toxic and Hazardous Materials Agency



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## Evaluation of Composting Implementation: A Literature Review

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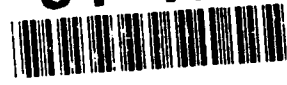
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EVALUATION OF COMPOSTING IMPLEMENTATION:  
A LITERATURE REVIEW

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## EXECUTIVE SUMMARY

An Evaluation of Composting Implementation: A Literature Review involved the following scope:

1. Composting technology was evaluated for the destruction of explosives wastes in soils.
2. Literature was reviewed from 1982 to the present by both manual and electronic searches of domestic and foreign literature.

Composting is a promising approach to the destruction of munitions wastes in soils. The technology can be cost effective, compared to physical destruction methods like incineration. In the early 80s, investigations of biological treatment of explosives waste suggested that many constituents were either innately recalcitrant or produced toxic intermediates of end products. These studies were conducted from an engineering perspective; direction from the life sciences was limited.

As biotechnology advanced, new organisms were isolated and utilized in bioremediation. Better control and monitoring processes were developed to optimize biological systems. With this approach, the definition of 'recalcitrant compound' changed. Degradation became no longer an innate quality of the chemical compound itself, but rather a function of the organisms and the optimization conditions used to assess degradability. Likewise, organisms were found that completely mineralized explosives wastes or degraded them to intermediates. These intermediates could be metabolized further by other members of the microbial community.

Recent studies from many laboratories offer significant proof of the degradation of explosives wastes without the production of toxic end products or recalcitrant intermediates. These recent developments support the continued development of bioremediation technology as planned for the Umatilla Army Activity Depot and for the extension of other biotechnology approaches for bioremediation of explosives wastes.

During the past 10 years, mathematical modelling of composting systems was evolved from simple, unidimensional models based on the hyperbolic function of Michaelis-Menton enzyme kinetics to more sophisticated, multivariant descriptions that integrate many physical, chemical, and biological components. While the approach to modelling is still empirical, the widespread use of commercial composting units for the treatment of municipal and industrial biosludge from wastewater treatment systems has provided the opportunity for model development and verification. Indeed,

composting technology has progressed significantly since the early static piles and windrows to large-scale, sophisticated, in-vessel systems. Models can now be used to predict degradation kinetics, compost quality, power consumption, and volatiles production.

The application of toxicity measurements to composting technology has focused on two general areas:

1. determining the absolute chronic and acute toxicity of munitions wastes and the products of composting; and
2. monitoring changes in toxicity during the composting process to assess loading capacity, system progress, and compost maturity.

Additional toxicity studies, in conjunction with the appropriate controls and analytical evaluations, are recommended for the new, optimized systems discussed above, to clarify the issue of previously reported toxic constituents. Since many of the organisms reported to mineralize explosives wastes can also use the waste as a sole carbon source, the accumulation of toxic, recalcitrant intermediates is unlikely.

## 1.0 INTRODUCTION TO SCOPE OF LITERATURE SURVEY

This literature review covers literature primarily from 1982 to the present. Selected earlier references are included to provide perspective for the discussion of model development and compost maturity. The search was conducted manually and by searching numerous electronic databases contained on the Dialogue database system. The survey includes both foreign and domestic literature.

The search was based on key terms, key authors, and key periodicals. The manual search also included the 'gray literature' of professional meetings, symposia, and workshops.

### Key terms included:

- trinitrotoluene (TNT)
- dinitrotoluene (DNT)
- nitroaromatic(s)
- explosives
- munitions
- pink water
- bioremediation/biodegradation
- composting

### Key Authors included:

- Bach, P. D.
- Epstein, E.
- Finstein, M. S.
- Kaplan, D. L.
- McCormick, N. G.
- Nakasaka, K.
- Sayler, G. S.

### Key Periodicals included:

- Journal of Fermentation Technology (Journal of Fermentation Engineering as of 1989)
- Biocycle
- Environmental and Applied Microbiology

In addition to the focused search on the degradation of explosives by composting, references relevant to the field demonstration of explosives composting at the Umatilla Army Depot Activity have been included. The general categories for these references are:

- systems for tracking microorganisms introduced into a composting system;

- vendor sources for producing commercial quantities of microorganisms for field inoculation;
- references in microbial ecology related to survival of introduced strains, inoculum density, and toxicity tolerance; and
- modelling for developing predictive systems for compost operations.

Two bibliographies are presented:

1. a list of references annotated, reviewed, and cited in this review; and
2. a supplemental bibliography of relevant references from the foreign literature discovered in this search, but not reviewed because of budget limitations for procurement and translation.



## 2.0 BACKGROUND OF COMPOSTING

Composting technology is based largely on an empirical approach to the intensively managed biodegradation of organic wastes (Biocycle, 1989; Brinton et al., 1988; DeBertoldi et al., 1987; Golueke, 1977; Haug, 1980; Razvi et al., 1989).

Historically, composting has been used to accelerate the biodegradation of a variety of organic wastes from agricultural products (Fujio et al., 1986; Knapp et al., 1983) to human wastes (Iacobini et al., 1984; Kuter, et al., 1988). In the municipal sector, large-scale composting units are well established for the routine treatment of biosludge from wastewater treatment plants (Satriana, 1974; USEPA, 1988). Composting technology has only recently been recognized as a potential treatment process for hazardous wastes (Mays et al., 1989).

Traditionally, the definition of composting has included the use of thermophilic conditions and thermophilic microbial consortia to biodegrade organic wastes in an enriched matrix of readily degradable organic substrates, bulking agents, nutrients and moisture (Elliot et al., 1988; Goldstein, 1988, 1989; Kuter et al., 1988). The process depended on the exothermic reactions of the microbial consortium and the insulating properties of the compost matrix to retain heat. Indeed, retention of the heat produced over a given time period eliminates human pathogens from the compost product (Burge et al., 1987; Culp et al., 1980; Millner et al., 1987).

More recent applications of composting technology to the field of organic wastes from industry have broadened the definition to include both thermophilic and mesophilic incubation conditions. Contaminated materials--soils, for example--are removed from their existing location and mixed with a supplemental carbon source, nutrients, and a bulking agent to increase porosity for improved gas exchange. The broader definition of composting differs from traditional land farming or land treatment technology in the amount of organic matter added to the treatment mixture. Composted systems contain significantly more organic matter (generally >20% w/w) than is generally found in soils (0 to 15% w/w). The supplemental organic matter serves as a substrate to support a diverse microbial consortium of aerobic and facultative anaerobic organisms. Regardless of the ratio of fixed solids to organic solids, the compost mixture can be managed in any of the traditional composting methods of windrow, static pile, or in-vessel treatment.

Static pile systems employ an aeration/heat management system to improve process control over the windrow system. An air exchange manifold of perforated or screened pipe is located under the pile.

The manifold is connected to mechanical blowers which may be activated by signals from temperature sensors and or gas probes in the pile and gas manifold system itself. Two approaches are documented in the literature: a vacuum approach (Finstein, 1989, Hagar et al., 1989), and a pressurized system (Epstein et al., 1979). The vacuum or suction approach pulls air in from the surface of the pile to maintain an aerobic environment and to adjust temperatures within the pile.

This approach has the following advantages:

- control of volatile emissions and odors;
- management of moisture by application to the pile surface; and
- good distribution of heating/cooling with minimal channeling in the pile.

The pressurized system provides air to the core of the pile. This approach has recently been commercialized for the control of volatile organic compounds from other processes. Furthermore, the biofilter or biopile has been used in Europe for odor control in municipal waste water treatment plants and industries for many years. This technology has been used domestically for odor control in urban wastewater treatment facilities (Epstein, personal communication). The pressurized system has the following advantages:

- rapid control of heating/cooling by directing air directly to the pile core; and
- useful for treating volatiles in the influent air stream.

Epstein (1979), in one of the early government-funded studies of composting of organics other than municipal sludge, found that bin composting accelerated the biodegradation of crude oil and number 6 fuel oil.

Optimum composting conditions include:

- temperature of 55°C;
- 40 to 60% moisture;
- carbon:nitrogen ratio near 30 to 1;
- sufficient aeration to maintain aerobic conditions;
- frequent mixing; and
- materials of high surface area.

### 3.0 REVIEW OF USATHAMA EXPLOSIVES-CONTAMINATED WASTE COMPOSTING EFFORTS FROM 1982 TO THE PRESENT

Early studies preceding those of Kaplan and Kaplan provided mixed results on the completeness of degradation. Some suggested that TNT and related compounds were not biodegradable (Nay et al. 1974) or produced degradation intermediates which accumulated, while others demonstrated near complete degradation (Klausmeier et al., 1974).

Osmon and Andrews (1978) conducted some rudimentary landfarming experiments on small plots amended with TNT with promising results. Unfortunately, plot operating conditions like pH, moisture, nutrient availability and mixing were not well defined and appropriate controls were not included. Of 10 treatment regimes, five achieved 65% or better reduction of TNT in 10 weeks of incubation. Similar degradation rates have been routinely reported for polynuclear aromatic hydrocarbons (PNAs), a subgroup of which includes nitrogen-containing heterocyclics.

In follow-on work to Osmon and Andrews (1978), who showed degradation of up to 10% dry weight TNT but did not study metabolic pathways, Kaplan and Kaplan (1982) found that thermophilic biotransformation of TNT (2,4,6-trinitrotoluene) followed the same transformation scheme reported for mesophiles. Nitro groups are reduced to amino groups without aromatic ring cleavage. Intermediates from the degradation of C<sup>14</sup> TNT accumulated in an insoluble, humus-like fraction.

Kaplan and Kaplan concluded that composting offers no advantage over mesophilic biodegradation because the thermophilic metabolic pathways produce the same toxic and mutagenic intermediates as the mesophilic ones. Composting incorporates these intermediates into the insoluble humic fraction.

Atlantic Research Corp. (1982) conducted bench-scale composting trials for degradation of TNT and RDX to determine:

- 1) degradation limits and kinetics,
- 2) relationships to scaled-up systems, and
- 3) leachability of TNT and RDX from the compost.

TNT was transformed more rapidly than RDX in all composting systems. Negligible labelled CO<sub>2</sub> was detected, indicating that mineralization through ring cleavage had not occurred, even though extractable TNT and RDX concentrations plummeted. The leaching study showed that composting initially increased the mobility of TNT, possibly due to biosurfactants, prior to rapid degradation.

Greene, et al. (1985) conducted soil column biodegradation studies with simulated pink water--a cocktail of TNT, RDX, HMX, and 2,4,-DNT. Explosives concentration, total organic carbon, nitrates, nitrites, ammonia, pH, redox potential, and biotransformation products were monitored weekly. The results indicate that land treatment/land farming is not an acceptable treatment option for pink water because of:

1. lack of biodegradation of some of the pink water constituents;
2. the generation and accumulation of potentially toxic intermediates and reaction products; and
3. the potential for additional contamination of groundwaters and soils.

General conclusions from these studies include the following:

- Supplemental carbon is not essential for the biotransformation of TNT. However, consistent with cometabolism expectations, it stimulated biotransformation.
- RDX and HMX were very mobile and leached readily in the column studies; no degradation of HMX was observed.
- Nitrates/nitrites were not found in the initial soil leachates, but were found at up to 40 ppm in the carbon-amended active columns. The columns with the highest microbial activity had the highest concentration of nitrate leachate. Ammonia was not detected in any systems.

Comments:

1. Inoculum was obtained from a municipal waste water treatment plant. Selection and acclimation periods were not considered.
2. Loading capacities were not adjusted to the microbial tolerance of the simulated pink water cocktail.

In addition to degradation of TNT by bacteria, degradation has recently been reported by the white rot fungus Phanerochaete chrysosporium (Fernando et al., 1990). Degradation was demonstrated by mass balance analysis, metabolite formation, and by mineralization of completely ring-labelled TNT to carbon dioxide in both liquid cultures and in soils. When TNT concentrations similar to those that might be found in water or in soil at contaminated sites were treated for 90 days, approximately 85% was degraded.

### 3.1 Feasibility Assessment of Composting Technology

Weston, R. F. (1985) conducted a literature overview in 1985 which indicated that landfarming technology was not acceptable for biodegradation of TNT, DNT, RDX, and HMX because of the dearth of published accounts of mineralization of these constituents. It was generally thought that the reduction of the nitro groups of TNT and DNT without aromatic ring cleavage produced toxic and mutagenic compounds which accumulated in the environment. Anaerobic degradation of RDX and HMX was reported, but was thought to be too slow and to produce potentially toxic nitroso compounds (in et al., 1984, 1990). Weston essentially eliminated landfarming as a feasible technology because of the following:

- general perception that the biodegradability of TNT, DNT, RDX and HMX is low (based largely on the work of Kaplan et al., 1982a,b,c; 1983; 1984; 1985a,b; 1989 and McCormick et al., 1981; 1984);
- variability in the optimum transformation conditions required for each constituent (TNT, DNT, RDX, HMX) precludes using a single system for all four;
- no published proof of mineralization of TNT, DNT, RDX, or HMX; and
- high potential for the production, accumulation, and mobilization of toxic and mutagenic intermediates.

Weston's (March 1989) field demonstration of composting at the Badger Plant focused on the degradation of nitrocellulose (NC)-contaminated soils. They reported significant reduction (99%) of relatively high loads of nitrocellulose (up to 60%) or NC-contaminated soils (up to 32%) in a series of static pile composting systems with aeration. Temperature and moisture variables were difficult to control. The production of toxic and/or mutagenic intermediates or end products was not explored.

Montemagno and Irvine (in USATHAMA, 1989) have explored the SBR (sequencing batch reactor) for degrading explosives-contaminated soils in a soil slurry reactor. The reactor employs alternating aerobic and anaerobic conditions to exploit respective metabolic pathways.

## 4.0 MODELLING OF THE COMPOSTING SYSTEM

### 4.1 Temperature and Mass Transport-Based Models

One of the earliest models with applications for composting systems was developed by Finger et al. (1976). The model was based on the measurement of temperature and oxygen distribution in a compost pile of ground corn husks, straw and race horse manure. For their experimental design, microbial growth was controlled by temperature and mass transfer within the compost pile. Using the model, they predicted the optimum pile size, compost matrix density (pore size), and external oxygen concentration.

- Static piles about eight feet high with a height to width ratio of 0.93 provided the optimum activity and uniformity.
- Matrix density had only an indirect effect on conserving temperature. Higher densities increased temperature and oxygen consumption.
- High external oxygen concentrations increased the reaction rates by reducing the compost uniformity. These observations were confirmed and extended by Bach et al. (1985) and Nakasaki et al. (1987), respectively. They demonstrated that bulk density influenced the reaction rate via temperature and oxygen consumption, because aerobic microorganisms, degrading organic matter in a compost pile, grow primarily on the macroscopic interface between solids and air.

Bach et al. (1987) and Nakasaki et al. (1987) refuted the earlier findings of MacGregor et al. (1981) in their evaluation of the thermal balance during the composting of sewage sludge. Their study in a commercial composting plant provided the most sophisticated model.

The primary objective of composting sewage sludge is to decrease the water content of the finished product. Secondary objectives include elimination of human parasites and pathogens by sustained heat treatment and reduction of organics. Temperature studies were done at a constant, low air flow and at a variable air flow designed to keep temperatures at 60°C. The thermal balance of the reactor was described by the equation stating:

Heat generated by the reaction equals:

heat removed by supplied air +  
latent heat removed by vaporization of water +  
heat loss from the wall of the reactor +  
net heat change of the reactant solids and the reactor.

Each of the above components was described by an individual equation. In both systems, about 20 kg of volatile matter was lost per kg mol of carbon dioxide evolved. About 15.3 kg of water was generated per kg mol of carbon dioxide. The dew point temperature of the exhaust gas was a function of the moisture content of the compost, not the air flow through the system. In addition to dew point temperature, other parameters were measured to monitor thermal balance in the reactor:

- air flow,
- air flow,
- concentration of carbon dioxide in the exhaust gas (represented in the equations as a molar ratio based on supplied air), and
- difference between the molar ratio of oxygen in the supplied air and that in the exhaust gas.

For mass balance calculations, the conversion of volatile (organic) matter was based on the concentration of carbon dioxide in the exhaust gas and the rate of air flow through the system. Thermal balance analysis provided a good description of the temperature and moisture content changes during the reaction. The total thermal balance in kcal per day was provided for the commercial reactor along with the relative contribution of each of the four components above. The thermal balance model was used to predict the balance in three type of reactors: laboratory scale; commercial-scale, open-bin type; and commercial-scale, multistage tower reactor.

#### 4.2 Enzyme Kinetics-Based Models

Whang and Meenagan (1980) proposed a model for composting systems, based on the Michaelis-Menten equation of enzyme kinetics first derived by Henry. The reaction mechanism for the composting process was considered to be an intermediate organism-substrate complex under quasi-equilibrium conditions. Two kinetic constants,  $K_1$  and  $K_2$ , were calculated in three experiments. Constant  $K_1$  represented the enzyme-substrate complex of Michaelis-Menten and was independent of the oxygen source (either air or pure oxygen gas). Constant  $K_2$  represented the kinetic variable in the system whose value was directly related to oxygen tension in the system.

## 5.0 CONSIDERATIONS OF TOXICITY IN COMPOSTING MUNITIONS WASTES

Griest et al. (1989) is continuing to evaluate the chemical and toxicological characteristics of both mesophilic and thermophilic composting products. They are identifying any toxic transformation products and assessing the potential for long-term release constituents bound in the humic fraction. Acute and chronic assays are being conducted with conventional indicator organisms including *Ceriodaphnia* and fathead minnow larvae. Bacterial mutagenicity is being tested by the Ames assay.

COMMENT: Toxicity screening should be an integral part of the optimization process in defining the treatment matrix for optimization. Parameters should be selected that foster toxicity reduction.

Atlantic Research Corp. (May 1986) conducted a series of bench-scale and pilot-scale composting trials with explosives-contaminated soils from Louisiana AAP (TNT, RDX, HMX and Tetryl) and Badger AAP (nitrocellulose). Carbon-14 labeled tracers were used to track biotransformation products.

Sewage sludge-based composts were more effective at degrading TNT and less loading rate sensitive than hay-horse feed based mixtures. Amino derivative transformation products did not accumulate; however, the ring cleavage was not significant and most of the label remained in the unextracted residue.

RDX was mineralized to carbon dioxide, but inhibited microbial activity at loading rates exceeding 10%. Like TNT, the hay-horse feed mixture was the most sensitive to loading rate.

HMX was better in the sewage sludge mixture than the hay-horse feed mixture, but only 30 to 50% reduction accrued in 10 weeks. Both composts were sensitive to loading rates of these sediments.

Tetryl was degraded effectively in both composting systems independently of loading rate. Labeled carbon was collected in both the unextractable residue and as carbon dioxide. Nitrocellulose was completely degraded to carbon dioxide and water.

Kaplan et al. (1985) studied the effects of initial loading rate, microorganism titer, temperature, moisture content, organic matter, and oxygen titer on the transformation of 2,4,6-trinitrotoluene in soils. Only the first three parameters had significant effects on the degradation rates. Microorganisms for this study were a mixed culture obtained from contaminated site soils, garden soils, and lake water. Increasing concentrations of TNT decreased trans-



formation rates; however, the lowest loading rate produced the most mono- and di-amine transformation products.

COMMENT: This system was not optimized for microbial activity, TNT degradation, or toxicity reduction. No data were collected on pH changes, nutrient flux, or oxygen demand.

Liu et al. (1990) have reported the relationship between toxicity and biodegradability by using DNT (2,4-dinitritoluene) as a model compound in an anaerobic system. In short-term bioassays with six defined, anaerobic bacteria, stable anaerobic transformation products of DNT (Liu et al., 1984) were more toxic than the parent compound. They concluded that the interpretation of short-term bioassay data may be complicated by biotransformation of the assay chemicals during the bioassay if a stable, nontransformable control is not included in the assay. Because of the relationship between toxicity and biodegradability, a short-term toxicity bioassay like the Microtox bioassay (Microbics Corp., Carlsbad, CA) would be useful in monitoring changes in toxicity during the biological treatment of explosives wastes.

## 6.0 OPTIMIZATION PARAMETERS FOR COMPOSTING

### 6.1 Bioaugmentation of Composting Systems

Weston's (1985) literature review did not consider bioaugmentation with selected microorganisms capable of mineralizing these constituents. Unkefer et al. (1989) reported a seven-member consortium capable of mineralizing TNT to carbon dioxide and growing on TNT as a sole carbon source. Culture of these organisms in defined media with completely ring-labeled TNT confirmed ring cleavage.

Subsequently, Unkefer (personal communication, 1990) isolated a single organism from the consortium capable of mineralizing TNT. This organism is a candidate for introduction into one of the composting vessels at the Umatilla Army Depot Activity.

Seeding composting systems is relatively recent in the literature. Nakasaki and Akiyama (1988) evaluated the seeding of composting household wastes by measuring changes in carbon dioxide evolution, temperature, conversion of volatile matter, pH, and microbial succession in the compost in both seeded and nonseeded systems. Seeded systems outperformed the nonseeded ones in all parameters, including final conversion of volatile matter.

Enhanced activity was noted on both the mesophilic and thermophilic stages of composting. A similar effect was not observed with sewage sludge, probably because of the high titer of endogenous organisms indigenous to the sludge. Seeding composting munitions waste should perform much like organic household wastes.

In any bioaugmentation system, inoculum size plays a major role in establishing the introduced culture(s) in the existing microbial population. Ramadan et al. (1990) evaluated the introduction of *Pseudomonas cepacia*, capable of degrading para-nitrophenol, into nonsterile lake water. Survival of the culture and subsequent degradation of the target compound was dependent on attrition related to protozoan predators and to the balance of essential nutrients in the water. Higher inoculum densities of up to  $4.3 \times 10^4$  provided sufficient survivors to degrade the target. At lower inoculum densities, supplemental nitrogen and phosphorus permitted degradation.

Sayler et al. (1986; 1988; 1989b; 1990) have provided an important summary of recent advances in biotechnology including:

- the development of biodegradative strains,
- gene probe methods for monitoring introduced organisms, and

- methods for monitoring, controlling and optimizing degradative strains during treatment.

Gene probe technology has been used extensively to confirm and track the persistence of microorganisms introduced into the environment (Jain, et al., 1988; Steffan et al., 1989a; 1989b).

Using gene probe technology, Jain et al. (1987) reported that microorganisms and plasmids introduced into groundwater aquifer material were maintained without specific selective pressure favoring the introduced species.

Similar technology has also been used to evaluate the microbial community diversity and species differences among communities (Ogram and Sayler, 1988; Sayler, et al., 1989a).

## 7.0 SUMMARY OF RESULTS AND CONCLUSIONS

### RECOMMENDATIONS

1. Further studies of composting should address the C:N ratio to account for the C:N ratio contributed by the TNT, DNT, RDX, and HMX. This will force the microorganisms to obtain their nitrogen from the munitions compounds rather than produce undesirable intermediates, from Greene et al., (1985).
2. Commission some optimized bench-scale biodegradations studies that employ N-15 labelled TNT, DNT, RDX, HMX, and/or NC to define the ultimate fate of the amino and nitro groups.
3. Many engineering studies omit essential biological considerations such as nutrient availability, consortium viability and activity, and changes in toxicity over time. These parameters must be an integral part of future and continuing engineering studies to assure activity and optimization of degradation kinetics.
4. Create a nomogram of [carbon], [nitrogen] and [phosphorus] to optimize the treatment system. A similar nomogram could be constructed based on volatile solids, fixed solids, and [nitrogen]. What is the magic C:N ratio for a given fixed solids concentration?
5. Composting occurs with high organic matter (OM) in the soil matrix. The cut off between high OM soils and low OM compost should be determined. What is the minimum [OM] for initiating the compost condition. What other variables effect this cut off?
6. Additional parameters should be analyzed for potential correlations with explosives concentrations as a surrogate for these expensive analyses. Indicator parameters might include:
  - oxygen uptake rate,
  - humification index,
  - toxicity (Microtox), and
  - UV/VIS scan.
7. How will the absence of recycle compost affect the degradation kinetics during the start up of a hazardous waste compost. Can the system kinetics be stimulated by recycled compost as is standard procedure in municipal systems? The potential lag phase must be considered in the overall kinetics calculations.

## APPENDICES

- 1.0 References Cited
- 2.0 Supplemental Bibliography

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